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CRYSTAL GROWTH OF: YTTRIUM PHOSPHATE CE3+:THORIUM
DIOXIDE CE3+:LANTHANUM ALUMINATE(U) PHILIPS LABS
BRIARCLIFF MANOR NY W ZWICKER ET AL. OCT 82

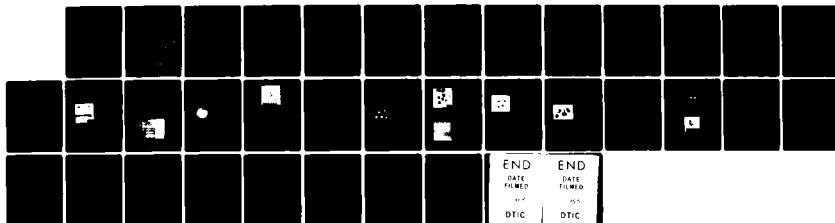
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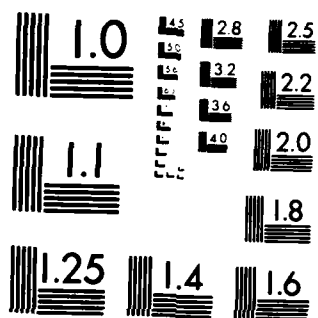
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CRYSTAL GROWTH OF:

YTTRIUM PHOSPHATE

Ce³⁺:THORIUM DIOXIDE

Ce³⁺:LANTHANUM ALUMINATE

PHILIPS LABORATORIES

A Division of North American Philips Corporation
Briarcliff Manor, New York 10510

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October 1982

Final Report for Period 15 February 1979 - 5 April 1982

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER	2. GOVT ACCESSION NO. AL-A122328	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) CRYSTAL GROWTH OF: YTTRIUM PHOSPHATE Ce ³⁺ :THORIUM DIOXIDE Ce ³⁺ :LANTHANUM ALUMINATE		5. TYPE OF REPORT & PERIOD COVERED Final Technical Report 15 Feb. 1979 - 5 Apr. 1982
7. AUTHOR(s) W. Zwicker S. Colak J. Khurgin		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS PHILIPS LABORATORIES A Division of North American Philips Corp. Briarcliff Manor, New York 10510		8. CONTRACT OR GRANT NUMBER(s) N00014-79-C-0180
11. CONTROLLING OFFICE NAME AND ADDRESS OFFICE OF NAVAL RESEARCH Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)		12. REPORT DATE October 1982
		13. NUMBER OF PAGES 33
		15. SECURITY CLASS. (of this report) UNCLASSIFIED
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) <div style="border: 1px solid black; padding: 5px; text-align: center;">DISTRIBUTION STATEMENT A Approved for public release; Distribution Unlimited</div>		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) crystal growth laser materials blue-green lasers laser polarizer materials Ce ³⁺ :thorium dioxide Ce ³⁺ :lanthanum aluminate yttrium phosphate		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Single crystals of YPO ₄ were grown from various types of fluxes, and their potential as polarizers in high power lasers was investigated. Although the crystals showed high resistance to damage by laser radiation, they were of poor quality due to cracks and flux inclusions. Crystals of Ce-doped ThO ₂ and LaAlO ₃ were grown by fluxed melt techniques using fluxes of various compositions. Standard absorption and luminescence techniques were used to evaluate the potential of these Ce-doped crystals for a solid state laser emitting in the blue-green region of the spectrum. No visible luminescence was observed from the crystals.		

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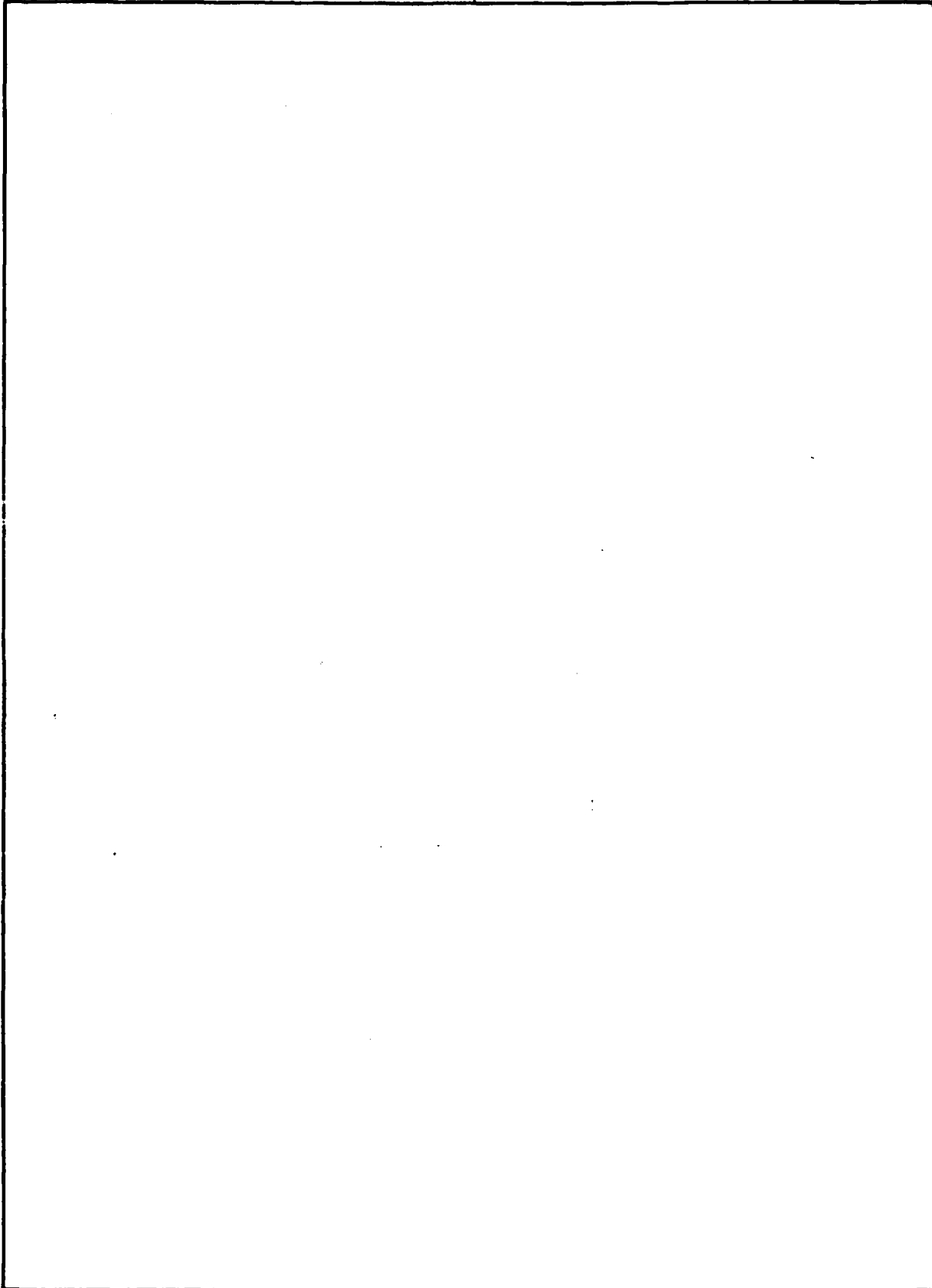
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SUMMARY

The goal of this contract was two-fold, viz., the growth of YPO_4 crystals of good optical quality and at least 5-6 mm in size (in all directions) for polarizers on high power lasers, and the growth of Ce^{3+} doped crystals of ThO_2 and LaAlO_3 for a solid state laser emitting in the blue-green region of the spectrum.

Crystals of YPO_4 were grown from various types of fluxed melts, and their resistance to laser radiation was investigated. Prismatic crystals up to 4 cm in length were produced, and the laser damage experiments indicated that such crystals withstood more intense laser irradiation than calcite which is presently used as polarizer. However, none of the YPO_4 crystals grown by us were free of flux inclusions and/or cracks.

Ce -doped ThO_2 crystals grown by us from fluxed melts were of nearly perfect cubic symmetry and up to 6 mm on a side. In order to force the Ce ions into the trivalent form, Ta^{5+} ions were added for charge compensation. Ce -doped LaAlO_3 crystals were grown from various fluxed melts; they were up to 7 mm on a side and similar to the ThO_2 crystals with nearly perfect cubic symmetry.

The crystals of Ce:LaAlO_3 and Ce:ThO_2 were examined by absorption techniques in the visible and near ultraviolet. Some samples were excited by various sources to check for luminescence. The results of these tests showed no luminescence corresponding to the observed broad absorption bands. This indicates that the cerium in these samples is either inactive (four valent) in the visible or its luminescence is totally quenched.

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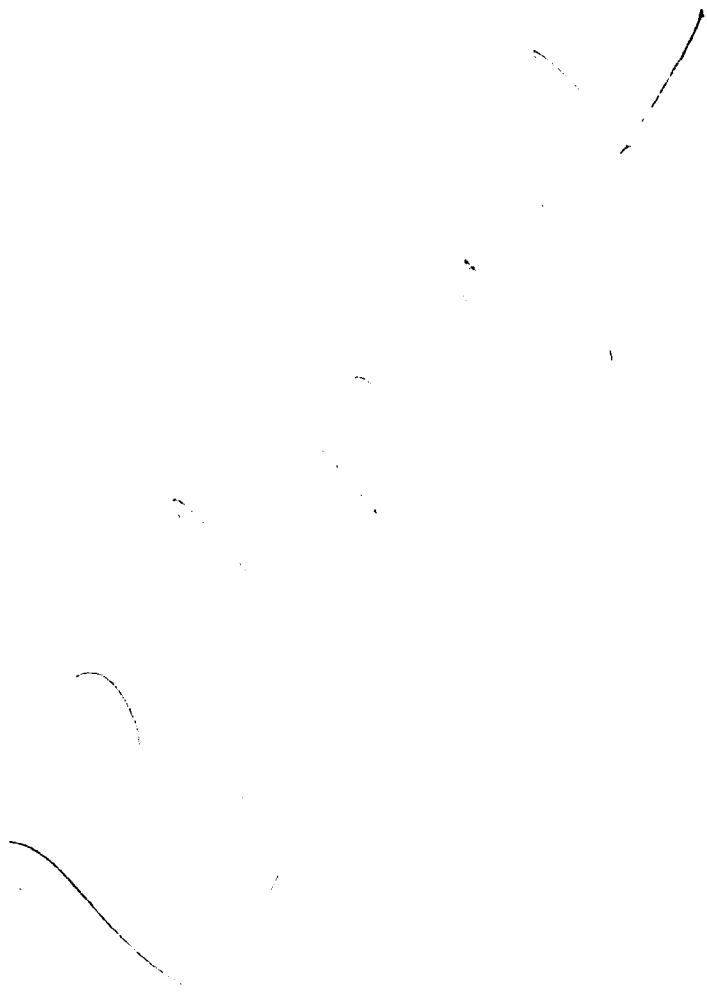
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1. INTRODUCTION

The goal of this program was two-fold, viz., the growth of crystals of YPO_4 of good optical quality and at least 5-6 mm in size (in all directions) for polarizers on high power lasers, and the growth of crystals of $\text{Ce}^{3+}:\text{ThO}_2$ and $\text{Ce}^{3+}:\text{LaAlO}_3$ for a solid state laser emitting in the blue-green region of the spectrum.

The optical and mechanical properties of the mineral calcite have made it the most important polarizer material for use in today's high-power laser systems. Although optical-grade single crystals of this mineral, up to 15 mm in diameter, were grown successfully in the laboratory (Ref. 1), no method for producing such crystals on an economically feasible scale has been found. All calcite crystals used for polarizers today are of natural origin and have to be imported to the United States. Optical-grade natural crystals, however, are becoming more difficult to find and as applications for lasers increase, the supply of the crystals is becoming more limited. Thus, the need for a replacement material with equivalent properties has become important. Yttrium orthophosphate (YPO_4) appears to fulfill these requirements; it was, therefore, that the growth experiments for single crystals of these compounds, described in this report, were undertaken.

The importance of an underwater or air-underwater blue-green laser link does not have to be emphasized here. Strong theoretical evidence exists that the Ce^{3+} ion in an appropriate host lattice could be lased efficiently at room temperature and that such a solid state laser may be tunable through the entire green region of the spectrum. It appears that both ThO_2 and LaAlO_3 may be such host crystals suitable for this application. This report describes our attempts to grow Ce^{3+} doped crystals of these compounds and some optical evaluation studies of such crystals.

2. MATERIALS CONSIDERATIONS

2.1 Yttrium Orthophosphate (YPO₄)

YPO₄ (xenotime) is tetragonal with $a = 6.88$, $c = 6.03$ kX, $Z = 4$ and is isostructural with ZrSiO₄ (zircon). It shows good [100] cleavage and is insoluble in water. Table 1 compares other pertinent properties of YPO₄ with those of some other polarizer materials.

TABLE 1. Properties of some polarizer materials.

<u>Polarizer</u>	<u>Structure</u>	At 589 nm:		<u>Mohs Hardness</u>	<u>Solubility in H₂O</u>
		n_e	$n_e - n_o$		
Calcite	Hexagonal	1.4865	-0.1720	3.	Low
Soda-Niter (NaNO ₃)	Hexagonal	1.2261	-0.2513	1.5-2.0	High
Zircon (ZrSiO ₄)	Tetragonal	1.968	+0.045	7.5	Low
Xenotime (YPO ₄)	Tetragonal	1.827	+0.107	4-5	Low

Calcite crystals of optical quality are extremely difficult to grow on a reproducible basis in the laboratory (Ref. 1). Soda-niter, which has an even greater birefringence than calcite, can readily be grown but is too soft to polish readily and is extremely soluble in water. It has never been seriously suggested for widespread use with lasers. Zircon, on the other hand, has been proposed (Ref. 2) as a laser polarizer. Its chief drawback is its relatively small birefringence, about one-fourth that of calcite. Xenotime has a birefringence twice that of calcite, has a reasonable hardness, is chemically rather inert, and small optically clear crystals of it were grown by various investigators in the past.

2.2 Ce³⁺:ThO₂

ThO₂ (thorianite) crystallizes in the fluorite structure with cations in high symmetry sites. Although Ce⁴⁺ fits these tetravalent cation sites, Ce³⁺ in ThO₂ may also be possible with charge compensation due to oxygen vacancies (Ref. 3). Addition of other foreign but optically inactive compensating ions such as Ta⁵⁺ may further help the incorporation of Ce³⁺. The bandgap of the ThO₂ host crystal is about $38,000 \text{ cm}^{-1}$.

However, if lead is present in the crystal, this edge decreases to about $28,000 \text{ cm}^{-1}$ (Ref. 4), which is low for pump bands of cerium ion. Cerium-related luminescence in ThO_2 has only been observed in candoluminescence form as bluish white light (Ref. 5). This luminescence is thought to be due to the electron transfer spectrum of Ce-O bands in ThO_2 .

2.3 $\text{Ce}^{3+}:\text{LaAlO}_3$

LaAlO_3 crystallizes in the Perovskite structure. Because of the long fluorescence lifetime of Ce^{3+} in this material compared to Ce^{3+} in other laser hosts, LaAlO_3 is considered a good candidate for a laser host. It has been reported that the excitation bands of cerium in LaAlO_3 are at 24200, 31200, and 40000 cm^{-1} (Ref. 6). Taking into account the Stokes shift in emission and the spin-orbit splitting in 2F_J ground manifold, then the fluorescence of Ce in this host is expected to be in the visible near the green region.

3. CRYSTAL GROWTH

3.1 Yttrium Orthophosphate (YPO_4)

Crystals of this compound had been synthesized a century ago (Refs. 7,8) by fusion of precipitated yttrium phosphate in potassium sulfate, borax, or salt of phosphorus and by fusion of yttrium oxide with potassium pyrophosphate (Ref. 9). More recently (Ref. 10), lead pyrophosphate was used as fluxed melt for the growth of YPO_4 crystals. This technique was used and improved by various investigators over recent years (Refs. 11-14). The largest crystals of YPO_4 resulting from these studies were about 1 x 4 x 15 mm in size but were usually not free of inclusions (Ref. 15).

During the first part of our experiments we grew crystals of YPO_4 from a fluxed melt of 86 mol % lead pyrophosphate ($\text{Pb}_2\text{P}_2\text{O}_7$) in which 14 mol % of yttrium oxide had been dissolved. This mixture was heated in a 100 ml, tightly covered platinum crucible inside a specially constructed flux growth furnace (see Fig. 1) at a rate of 300°C/h , until the upper surface of the melt reached 1400°C . The temperature was held constant at this point for

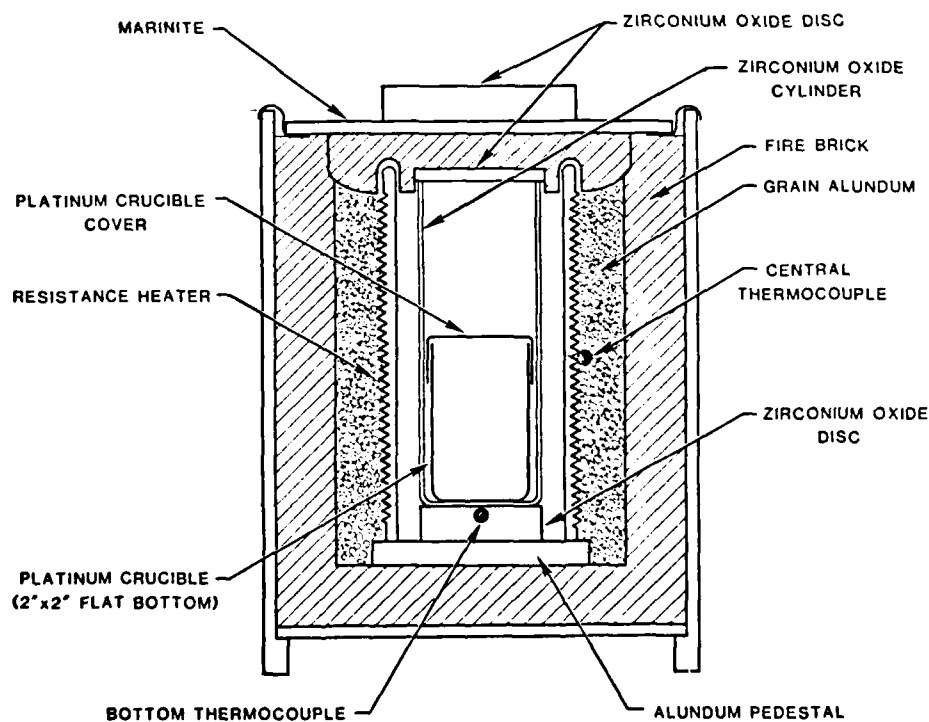


Figure 1. Schematic of high temperature flux furnace.

2-6 h, with the bottom of the crucible 80°C cooler than the surface of the melt. The surface temperature was then lowered to 970°C at a rate of 4°C/h, maintaining the 80°C vertical gradient throughout the five-day cooling period. The crucible was then furnace-cooled to 100°C.

Crystals were removed from the flux by soaking in hot water. Blade-like specimens measuring 15 x 3 x 0.7 mm were common. The optic axis was found to lie parallel to the 3 mm dimension. The largest faces were optically smooth and could thus be used without polishing for spectroscopic and damage experiments. Only a few of these crystals were free of inclusions (see Fig. 2).

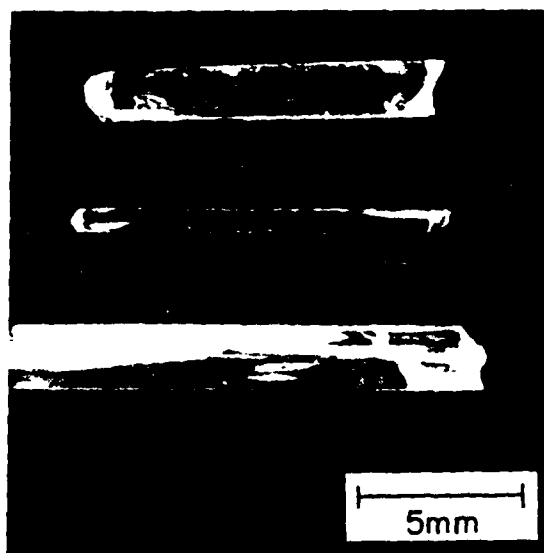


Figure 2. Single crystal platelets of YPO₄

However, during a visit of Dr. V.O. Nicolai from ONR to Philips Laboratories on August 28, 1979, we were able to deliver to him several optically clear crystals of YPO₄, averaging 15 x 3 x 1 mm in size, for laser damage experiments. Results of these experiments are described in Section 4 of this report.

In subsequent growth experiments various amounts (10-30 mol %) of PbO were added to the Pb₂P₂O₇ flux. PbO not only reduced the saturation temperature of YPO₄ (see Fig. 3) but also reduced the evaporation rate of lead from the fluxed melt. These experiments resulted in crystals in the form of needles or platelets up to 40 mm in size which is larger than any previously reported in the literature (see Fig. 4). None of these crystals,

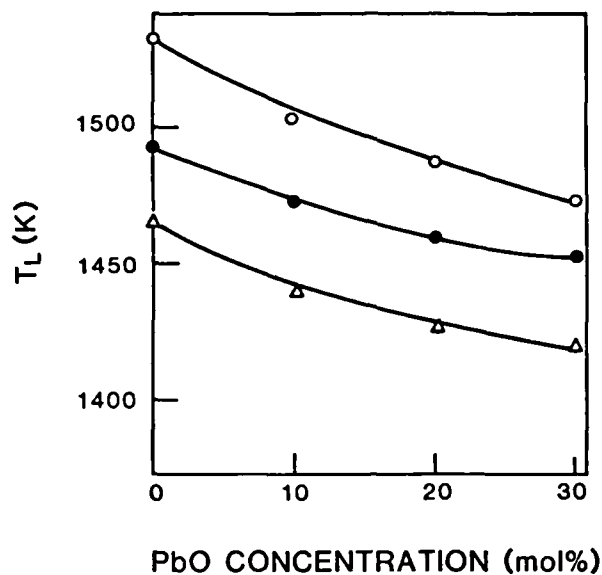


Figure 3. Saturation temperatures of various YPO_4 concentrations as a function of additional PbO in Pb_{22}O_7 . ○ 15, ● 14, and Δ 12 mol % YPO_4 (Ref. 16).

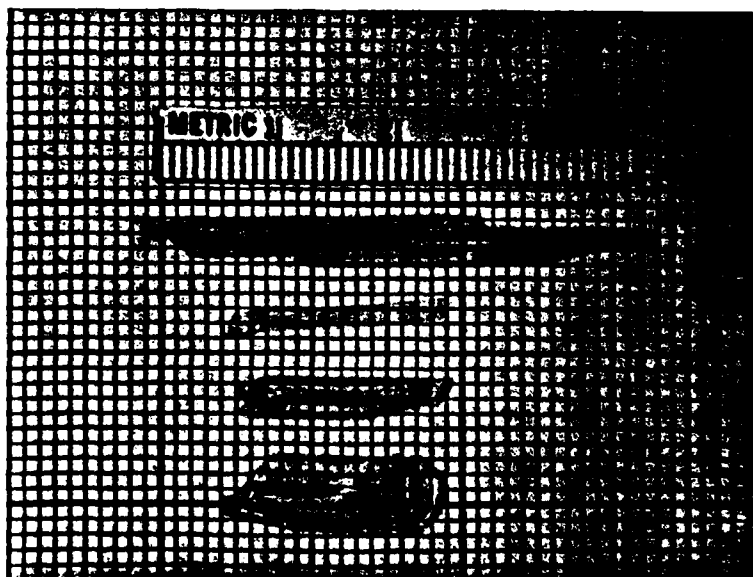


Figure 4. Single crystal needles or platelets of YPO_4 .

however, were totally free of cracks and/or inclusions. This confirms previous findings described in the literature. Cleavage cracks parallel to the (100) plane seem to form even prior to solidification of the flux since many contained flux inclusions. Fabrication of such crystals is thus extremely difficult and often not possible.

Since some cracking in the crystals may have been caused by solidifying flux, we attempted to separate the hot flux from the crystals with the help of a platinum screen mounted inside the crucible, as shown in Figure 5, on top of the fluxed melt. After completion of the crystal-growth run,

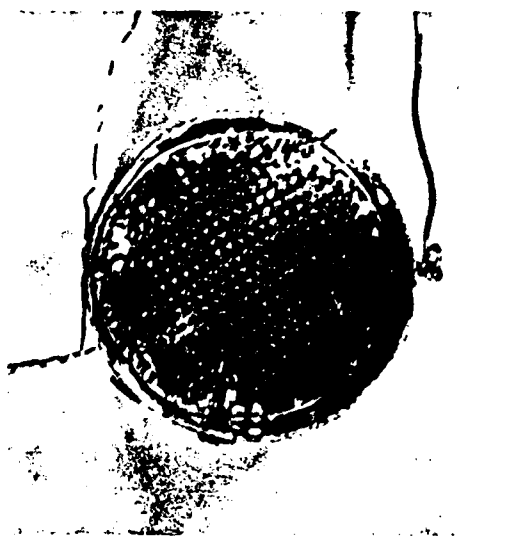


Figure 5. Platinum crucible with platinum screen insert for separating YPO_4 crystals from the hot flux.

the crucible was inverted and the crystals collected on the screen while the hot flux ran through it and collected on the cover of the crucible. These experiments, however, were only partially successful since the crystals still showed flux inclusions (see Fig. 6).

We were able, nevertheless, to fabricate a prism ($\sim 2 \times 2 \times 6$ mm) from one of those crystals. The prism was delivered to ONR in November 1980 (Sample #11) for further evaluation. This prism was also not optically perfect, since it showed again some cleavage cracks partially filled by flux, as mentioned above.



Figure 6. YPO crystals separated after growth from the flux by a platinum screen. (scale = mm)

Growth experiments using a mixture of Y_2O_3 - PbF_2 - PbO - MoO_3 and P_2O_5 with a mol ratio of 2.5 : 29.6 : 27.9 : 24.4, and 9.6% as flux resulted in larger (4-5 mm diameter) crystals of polyhedral shape. Although these crystals showed somewhat less of a cleavage problem, flux inclusions were even worse and no effort was made, therefore, to fabricate prisms from the crystals.

It was recognized at that point that although it might be possible to produce some small prisms from such crystals of YPO_4 , none of the processes used were suitable for larger scale production. We were asked, therefore, by ONR to discontinue this effort by the end of 1980.

3.2 Ce^{3+} : Thorium Oxide (Ce^{3+} : ThO_2)

Thorium-dioxide single crystals of significant purity are not found in nature, nor have laboratory syntheses prior to 1964 produced crystals of the size and perfection acceptable for studies concerning this exceptional refractory oxide. Nordenskjold and Chydenius (Ref. 17) and Bahr (Ref. 18) recrystallized ThO_2 as tetragonal crystals by heating it with $Na_2O \cdot 2B_2O_3$ in a pottery oven. Variations of this method were used by Goldschmidt and

Thomassen (Ref. 19) and by Weaver et al. (Ref. 20). Crystals of ThO_2 were also grown from K_3PO_4 by Ouvrard (Ref. 21) and from $\text{Na}_2\text{CO}_3\text{-ThF}_4$ by Duboin (Ref. 22). Liebmann (Ref. 23) reported growth of ThO_2 needles upon heating polycrystalline ThO_2 near its melting point. ThO_2 crystals exceeding 1 cm^3 in volume have been routinely produced in an electric arc furnace, but their purity is questionable (Ref. 24). Specimens of the arc-grown crystals are opaque, discolored red to black, and show poor facial development (Ref. 25).

The first successful growth of ThO_2 crystals from fluxed high-temperature melts (Ref. 26) was achieved from PbO-PbF_2 , $\text{Bi}_2\text{O}_3\text{-PbF}_2$ and PbF_2 flux systems. Later, other flux systems such as $\text{Li}_2\text{O-2WO}_3$ (Ref. 25); $\text{PbO-PbF-B}_2\text{O}_3$, $\text{Na}_2\text{O-MoO}_3\text{-B}_2\text{O}_3$ and $\text{Li}_2\text{O-MoO}_3\text{-B}_2\text{O}_3$ (Ref. 27); $\text{Na}_2\text{O-B}_2\text{O}_3$ (Ref. 28); $\text{PbO-V}_2\text{O}_5$ and $\text{B}_2\text{O}_3\text{-V}_2\text{O}_5$ (Refs. 29 and 30) have been used successfully. It is only recently that ThO_2 crystals have been grown from the melt, using the cold-crucible (skull melting) technique (Ref. 31).

After studying previous crystal growth efforts and after performing some preliminary tests, we decided to use certain flux systems for the growth of Ce doped ThO_2 crystals. Compositions of these fluxes are summarized in Table 2.

TABLE 2. Compositions of most important fluxed melts used for growth of Ce doped ThO_2 crystals.

Mol %	Run No.							
	11+12	13	22	R-1	R-2	R-3	R-4+5	R-6
ThO_2	7.3	10.0	17.0	17.0	16.9	16.9	16.9	16.9
CeO_2	0.02	0.02	0.15	1.9	-	-	-	-
Ta_2O_5^*	0.38	0.38	0.85	-	0.2	0.6	0.3	-
Bi_2O_3	8.3	-	-	-	-	-	-	-
PbF_2	84.0	89.6	-	-	-	-	-	-
B_2O_3	-	-	60.0	60.0	59.8	59.8	59.8	59.8
BaO	-	-	15.0	14.5	14.8	14.8	14.8	14.8
BaF	-	-	7.0	6.6	6.6	6.6	6.6	6.6
CeF_3	-	-	-	-	1.7	0.13	0.06	0.06

R = Run in a reducing atmosphere (forming gas).

* Added for charge compensation

Growth was performed in tightly covered 100 cc platinum crucibles in flux furnaces similar to the one shown schematically in Figure 1. The temperature was raised to a homogenization temperature of 1150 to 1350 °C and kept there for at least 3 hours. For temperatures above 1200°C, furnaces with platinum resistance heaters were used. After equilibration of the melt, the temperature was lowered to the growth temperature which was generally 50°C below the homogenization temperature. Growth was achieved by lowering the growth temperature at a rate of 1 to 2°C/hour over a period of 4 to 6 days. Subsequently the melt was quenched and the crystals freed by dissolving the flux in dilute nitric acid. At the beginning of these experiments all growth was performed in air; during the latter part (runs marked with R in Table 2) a reducing atmosphere (forming gas with 2% hydrogen) was used. The crystals in Run #11 were brown (see Fig. 7), presumably due to lead impurities.

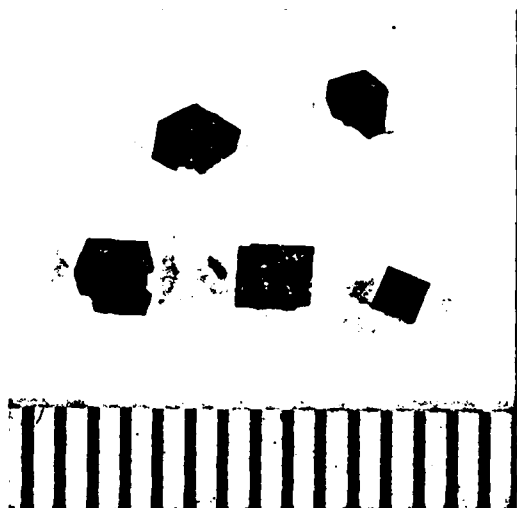


Figure 7. ThO_2 crystals grown from a $\text{Bi}_2\text{O}_3\text{-PbF}_2$ flux (Run #11) with substantial flux evaporation. (scale = mm)

Most of the lead fluoride was lost during this run, and the crystals therefore grew relatively fast. To prevent or reduce this evaporation, a tight fitting cover was used in the subsequent runs.

Run #12 produced crystals from a flux identical to that of Run #11 (see Table 2) except that these crystals were nearly colorless with a slight yellowish tint. Most of these crystals showed a nearly perfect cubic habit and were 2-3 mm in size; however, some were as large as 5 mm (see Fig. 8). Most of them showed some cracks and flux inclusions but were suitable for luminescence studies. About two dozen of the crystals were submitted to

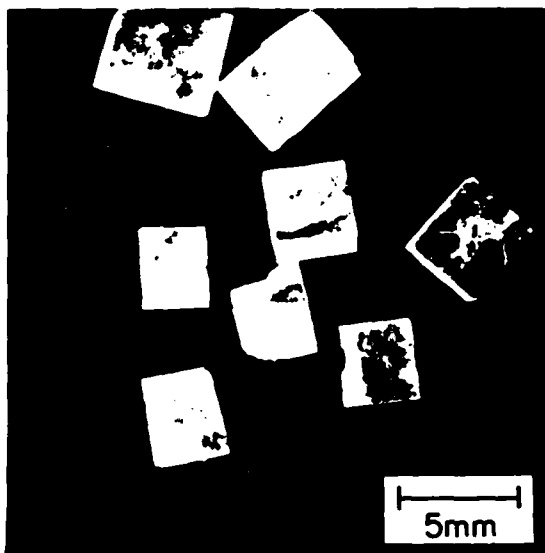


Figure 8. ThO_2 crystals grown from a $\text{Bi}_2\text{O}_3\text{-PbF}_2$ flux (Run #12) with little flux evaporation.

ONR on November 21, 1980 for evaluation. Since the platinum crucible was visibly attacked by Bi_2O_3 during the previous runs, it was eliminated from the flux used for Run #13 and all following runs. Run #13 produced crystals up to 6 mm on a side. These crystals showed a slightly less well developed crystal habit but they were clear and contained very few inclusions (see Fig. 9). They did show cracks, however, which may have developed when the flux contracted on cooling after and during its solidification.



Figure 9. ThO_2 crystals grown from a PbF_2 flux (Run 13). (scale = mm)

Since none of the Ce:ThO_2 crystals produced from lead-containing fluxes showed any visible fluorescence, it was assumed that lead impurities may cause quenching of the fluorescence. We grew, therefore, crystals from a BaO , BaF and B_2O_3 containing fluxed melt. Run #22 produced the best crystals from this series of runs (see Fig. 10). Unfortunately, these



Figure 10. Heavily cracked ThO_2 crystals grown from a B_2O_3 - BaO - BaF flux (Run #22). (scale = mm)

crystals were severely cracked since this flux contracted on cooling even more than the lead containing fluxes, thereby crushing the crystals suspended in the flux. Although there are techniques which allow separation of the crystals from the flux prior to cooling, we did not attempt to apply them after it was determined that the crystals did not show any visible fluorescence.

It was assumed at this point, that the reason for this lack of visible fluorescence may be that Ce was incorporated in these ThO_2 crystals in the four rather than the trivalent state, although the oxide was added for charge compensation.

It was decided, therefore, to use a reducing (forming gas with 2% hydrogen) furnace atmosphere, rather than air, for the following experiments. Both the platinum crucibles as well as our previously used flux furnace could not be used for these experiments. We acquired, therefore, a new type of high temperature furnace with molybdenum disilicide heating elements, which can be used with a reducing atmosphere. Vitreous carbon crucibles were used for the following growth experiments (marked with R in Table 2). In Run #R-1, Ce

was still added to the flux in the form of CeO_2 . The resulting crystals were small (0.5 mm) and of red color. Since they again showed no visible luminescence, it was decided to add Ce in the following runs in trivalent form, i.e., in form of CeF_3 rather than four valent as in CeO_2 . All of the crystals in the following four runs were small (1 mm or smaller) and of greenish color. Although the Ce concentration was varied substantially (see Table 2) and although the presence of Ce in these crystals was confirmed by energy dispersive X-ray fluorescence analysis (EDX), none of these crystals showed visible fluorescence. Run No. R-6, the last and final run, produced somewhat larger crystals (up to 2 mm in size) (see Fig. 11) but they again showed no visible fluorescence.



Figure 11. Crystals of ThO_2 grown from a B_2O_3 -BaO-BaF₂ flux in a reducing atmosphere. (scale = mm)

3.3 Ce^{3+} : Lanthanum Aluminate (Ce^{3+} : LaAlO_3)

There is no known natural mineral of the composition LaAlO_3 , and very little work on the growth of single crystals of this compound has been reported in the literature. The reason for the latter may be that the phase transition which this compound exhibits at 435°C presents a problem for growing it as a single crystal by many of the popular growth techniques. Single crystals have reportedly been grown, nevertheless, from fluxed solutions containing Bi_2O_3 and B_2O_3 to which La_2O_3 and Al_2O_3 had been added (Ref. 32). Seeded growth, using a hydrothermal synthesis process has also been reported (Ref. 32).

Single crystals of LaAlO_3 also have been grown by pulling from the melt (Ref. 33) at $\sim 2080^\circ\text{C}$.

We grew crystals of Ce doped LaAlO_3 from a $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ and a $\text{PbO-PbF}_2\text{-V}_2\text{O}_5$ flux to which in some experiments Ga_2O_3 or Sc_2O_3 had been added to replace Al partially in the lattice. The composition of the fluxed melts for four runs which produced the best crystals are listed in Table 3.

TABLE 3. Compositions of the most important fluxed melts used for growth of Ce doped LaAlO_3 crystals.

Mol %	L-1	L-6	L-7	L-9	L-13
La_2O_3	10.02	8.0	9.98	9.0	6.0
Al_2O_3	6.64	6.6	8.0	10.1	6.5
CeF_3	0.002	-	-	-	0.02
Bi_2O_3	63.99	64.2	64.0	64.7	-
B_2O_3	16.05	16.0	16.0	16.2	-
PbO	-	-	-	-	46.5
PbF_2	-	-	-	-	39.0
V_2O_5	-	-	-	-	1.98
Ga_2O_3	3.3	3.2	-	-	-
Sc_2O_3	-	-	2.0	-	-
CeO_2	-	2.0	0.02	-	-

LaAlO_3 crystals grown from Bi_2O_3 containing fluxes were yellow in color, which indicated incorporation of Bi in the lattice. All growth runs with this type of fluxes required a fast cooling rate (4°C/hr) because of the fast evaporation rate of the flux. Growth was performed between 1200 and 1000 $^\circ\text{C}$. After quenching, the flux was dissolved in dilute nitric acid. The resulting crystals generally were platelets up to 6 x 6 x 1 mm in size (see Fig. 12a). Run #L-1, however, produced a 7 mm large crystal of nearly perfect cubic habit (Fig. 13) but not free of inclusions. This crystal was transmitted to ONR on October 2, 1981 for evaluation. While this crystal grew at the bottom of the crystals, the platelets grew on the top of the fluxed melt. Although the platelets were for most part clear, they showed at least one inclusion in the center, probably at the original nucleation site.

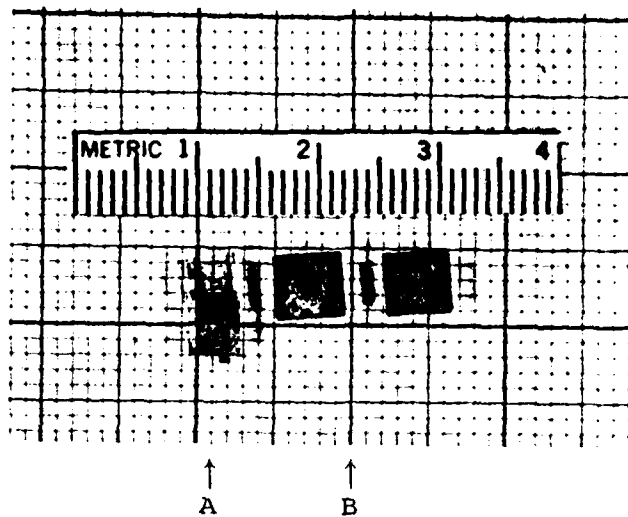


Figure 12. Crystals of LaAlO_3 in form of platelets.
 (a) grown from a $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ flux and cubes
 (b) grown from a PbO-PbF_2 flux.

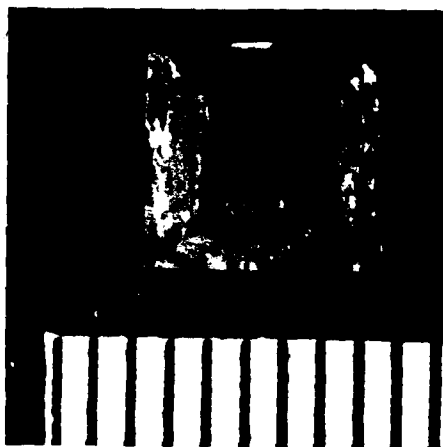


Figure 13. Single crystal cube of LaAlO_3 grown from
 a $\text{Bi}_2\text{O}_3\text{-B}_2\text{O}_3$ flux at bottom of crucible.
 (scale = mm)

Crystals of LaAlO_3 grown at the bottom of the crucible from lead-containing fluxes showed, again, a nearly perfect cubic habit (Fig. 12b)). The crystals were up to 5 mm on a side and brownish in color. They were grown again between 1200 and 1000°C. Crystals grown with a cooling rate of 4°C/hr were lighter in color than those grown with a 2°C/hr cooling rate, indicating that less lead was incorporated into the lattice. Crystals grown with slower cooling, on the other hand, showed less inclusions and surface defects. Optical and surface quality of crystals grown from Bi containing fluxes was superior to those of crystals grown from Pb containing fluxes.

Since none of the crystals produced from the fluxes listed in Table 3 showed visible fluorescence, it was decided to grow crystals of LaAlO_3 in a reducing atmosphere. Since none of the fluxes listed in Table 3 could be used with a reducing atmosphere, we attempted the growth from the following flux systems: $\text{KF-B}_2\text{O}_3$, $\text{NaF-B}_2\text{O}_3$ and $\text{BaO-B}_2\text{O}_3$, however, no crystals could be produced from any one of these fluxes.

4. CRYSTAL EVALUATION

4.1 Yttrium Orthophosphate (YPO₄)

Spectroscopic studies and laser damage measurements were performed at the Naval Research Laboratory on crystals of YPO₄ grown at PL. The results of these investigations had been published previously (Ref. 34) but are reported here again for completeness of this report.

Ultraviolet, visible, and infrared absorption spectra were determined with a 0.7 mm-thick YPO₄ crystal. Surfaces were as grown. Surface contaminants were removed by rinsing with isopropyl alcohol just prior to measurement. Spectra were recorded in the 210-2000 nm range on a Cary Model 17 spectrophotometer. From 2.5 to 8.0 μm , spectra were recorded on a Perkin Elmer Model 283B spectrophotometer. All spectra were obtained with unpolarized light.

As shown in Figure 14, the region of greatest transparency extends from 800 to 3000 nm. There are two prominent absorption bands near 2000 cm^{-1} and 3000 cm^{-1} . These appear to be overtones of the 1000- cm^{-1} fundamental absorption, ascribed to P-O vibrations in the phosphate ion (Ref. 35).

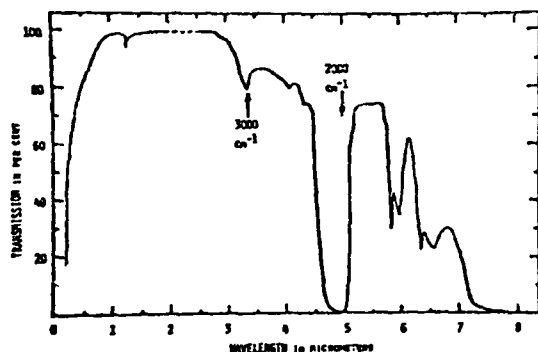


Figure 14. Transmission spectrum of YPO₄ (Ref. 34).

Q-switched pulses from a 100-mJ Nd:glass laser were used for damage studies; the pulse length was 17 ns (FWHM). The beam was focussed to a 0.025 cm (FWHM) spot at the front surface of the sample by placing the sample 15 cm behind a plano-convex lens whose focal length was 18 cm. Polarization was parallel to the long crystal dimension for some measurements, and perpendicular for others.

No damage was observed in YPO_4 unless accompanied by electrical breakdown of the air at the front surface. Damage was difficult to detect without a microscope. Only the front surface was damaged at low power densities, but both front and back surfaces were pitted at high power densities. For a given power density, occurrence of two-sided damage was somewhat dependent on polarization. With polarization parallel to the long (15 mm) dimension, two-sided damage took place about 90% of the time. With polarization parallel to the short (3 mm) dimension (the optic axis), two-sided damage was found only about 75% of the time. No difference was detected between results of N-on-1 and 1-on-1 studies.

For comparison, two types of calcite specimens were also subjected to damage. One group consisted of cleaved pieces of about the same thickness as the YPO_4 specimens. The surfaces of these had visible steps on them, which sometimes could not be avoided by the beam. The other group was a series of thicker slices cut from a calcite polarizer assembly. These were then polished on a wax lap with $0.03 \mu\text{m}$ aluminum oxide (Linde A), using triacetin as a lubricant. Results are shown in Table 4.

TABLE 4. Damage with 17 ns pulses of $1.06 \mu\text{m}$ radiation.

Crystal:	YPO_4	CaCO_3	CaCO_3
Surface:	As-grown	Cleaved	Polished
Thickness (mm)	0.7	0.6-0.7	1.4
Power density (GW/cm^2)	Occurrence of damage		
Under 2.0	Never	Frequent	Rare
2.1-2.4	Never	Certain	Frequent
2.5-3.0	Occasional	Certain	Certain
3.1-3.5	Frequent	Certain	Certain
Over 3.6	Certain	Certain	Certain

As the table shows, the yttrium orthophosphate crystals appear to withstand more intense irradiation than the calcite specimens. Further measurements on larger crystals of YPO_4 and on optically finished calcite will be needed to establish this conclusion.

4.2 Ce:LaAlO₃ and Ce:ThO₂

The optical evaluation of the LaAlO₃ and ThO₂ crystals doped with Ce was done by room temperature absorption spectra and by luminescence experiments at various temperatures with various excitation sources.

It was observed during these studies that crystals of ThO₂ produced from a PbF₂ flux (e.g., Run #13) turned dark brown within seconds after being exposed to 3638 Å radiation of our argon laser. This was due to formation of color centers. The crystals bleached to their original color after a few days, particularly when stored in darkness. Crystals of ThO₂ grown from a Bi₂O₃ and PbF₂ containing flux (Runs #11 and 12) showed a similar discoloration when exposed to the same type of radiation. However, they did not bleach even after being stored for over a year.

Transmission spectra of all types of crystals doped with Ce were obtained in the visible and near ultraviolet at room temperature by using a Beckman DK-22 spectrophotometer. Due to the small size of some samples and due to inclusions in some of them, the maximum transmissions through these samples were low. Typical examples of the results of these transmission measurements are given in Figure 15 for four different sample types. The preparation procedures for these samples are described in previous sections. As seen from Figure 15, all of these samples have a band edge between 500-700 nm after which the transmission decreases considerably. In addition to this edge, ThO₂:Ce crystals show a double peaked absorption nature with a dip slightly above 400 nm.

For study of the luminescence properties, the samples were excited with various optical sources (Ar⁺ 365 nm laser, Ar⁺ 515 nm, mercury lamp with monochromator between 300-400 nm) and with an electron beam (only ThO₂ samples in SEM). Some of the experiments with 365 nm excitation was done at 5°K. Luminescence was checked either visually or with a monochromator/photo-multiplier combination. In general, no luminescence was observed except for some extremely weak bands which could not be attributed to Ce luminescence.

It is seen from the above experimental results that the transmission spectra obtained from the samples show generally featureless and rather broad

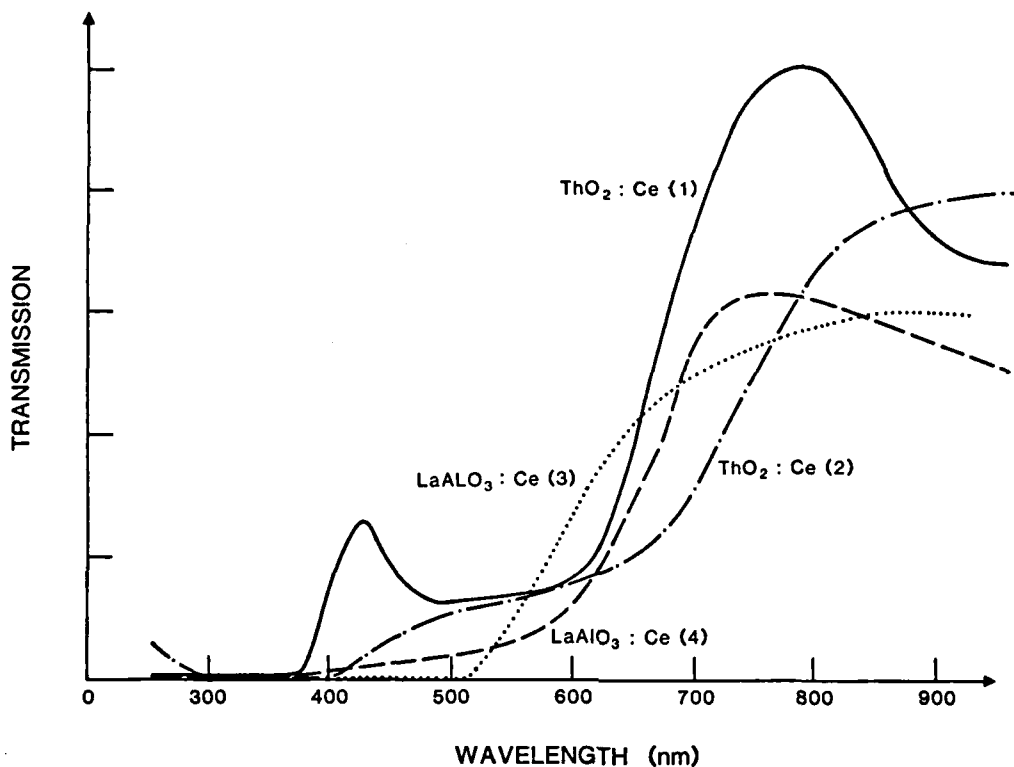


Figure 15. Transmission spectra of Ce:LaAlO₃ and Ce:ThO₂ samples grown from (1) Pb, (2) Bi and Pb, (3) Pb, and (4) no Pb containing fluxes.

absorption bands. The absorption bands did not produce any corresponding luminescence. If the bands belong to Ce³⁺ (no near visible absorption bands are expected for Ce⁴⁺), the above results show that Ce³⁺ are located at various sites in the crystal (possibly associated with other defects and impurities) thereby giving these broad absorption bands, and the luminescence for Ce³⁺ ions are totally quenched. These absorption bands may also belong to other impurities or defects which are completely unrelated to the Ce ion. In this case, cerium may perhaps be in four-valent form (Ce⁴⁺) which is an ion with no expected activity near the visible spectrum.

5. CONCLUSIONS

Highly birefringent crystals of YPO_4 of prismatic shape can be grown up to 4 cm in length by fluxed melt techniques. Such crystals showed a higher resistance to intense laser irradiation than calcite which is presently used as a laser polarizer. However, none of these crystals were free of cracks and/or flux inclusions, and it appears doubtful that such crystals can be grown on a commercial basis by fluxed melt techniques of a quality suitable for optical applications.

Cerium-doped crystals of ThO_2 and LaAlO_3 of cubic symmetry up to 7 mm on a side can be grown from fluxed melts. Although such crystals, from theoretical considerations, are expected to show strong luminescence in the blue-green region of the spectrum generated by Ce^{3+} ions, none of the crystals studied showed any visible luminescence. This indicates that cerium ions in the crystals are either inactive (four valent configuration) or their luminescence is quenched.

While it may be very difficult to incorporate Ce^{3+} into the ThO_2 lattice, it should be possible in the LaAlO_3 lattice. Since LaAlO_3 crystals can be grown from the melt in a reducing atmosphere, it seems more likely that such Ce^{3+} doped crystals may exhibit the visible luminescence expected from theoretical considerations.

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